Small samples of monomeric decamethylene, dodecamethylene, tridecamethylene, and tetradecamethylene carbonates were heated for twenty hours at 200° together with parallel samples each containing a trace of potassium carbonate. The uncatalyzed samples of tridecamethylene and tetradecamethylene carbonates showed a considerable increase in viscosity; the decamethylene and dodecamethylene carbonates a much larger increase. The catalyzed samples of decamethylene and dodecamethylene carbonates were completely changed to solid, waxy polymers; while the catalyzed samples of the other two esters were still semi-solid.

Samples of dimeric hexamethylene and decamethylene carbonates, both with and without traces of potassium carbonate, were heated for eight hours at 200°. The catalyzed samples changed to very viscous liquids which solidified to hard waxes; the uncatalyzed samples were unchanged.

## Summary

By heating linear polyesters with catalysts under certain conditions it is possible in many cases to bring about a smooth depolymerization to the corresponding monomeric and/or dimeric esters. This method makes it possible for the first time to prepare macrocyclic esters in good yields. Thirty new macrocyclic esters are described, mostly esters of dibasic acids. The cyclic carbonates and oxalates are obtained most easily. The ratio in which the two forms, monomer and dimer, are obtained is determined in part by the experimental conditions and in part by the nature of the ester—especially by its unit length. Monomers of 7 to 12 atoms are especially difficult to obtain.

WILMINGTON, DELAWARE

RECEIVED SEPTEMBER 2, 1933
PUBLISHED DECEMBER 14, 1933

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[CONTRIBUTION NO. 133 FROM THE EXPERIMENTAL STATION OF E. I. DU PONT DE NEMOURS & COMPANY]

# Studies of Polymerization and Ring Formation. XXI. Physical Properties of Macrocyclic Esters and Anhydrides. New Types of Synthetic Musks

BY JULIAN W. HILL AND WALLACE H. CAROTHERS

**Odors.**—The monomeric cyclic anhydrides and cyclic esters described in the two preceding papers have highly characteristic odors. In particular some of the higher members have odors closely resembling musk. This observation is especially interesting because of the bearing of odor on the general problem of macrocyclic compounds.

The essential principles of musk and civet are the macrocyclic ketones I and II. Ruzicka's demonstration[1] of this fact was followed by the discovery[2] that the lactones III and IV are odorous principles of angelica oil and musk-seed oil. These materials are highly valued as perfume ingredients. In spite of the great difficulties involved in their synthesis, a

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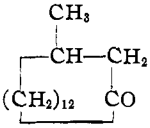
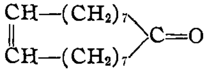
[1] Ruzicka, *Helv. Chim. Acta*, **9**, 230, 716, 1008 (1926).

[2] Kerschbaum, *Ber.*, **60**, 902 (1927); Ruzicka and Stoll, *Helv. Chim. Acta*, **11**, 1159 (1928).

synthetic ketone ("Exaltone," cyclopentadecanone) and a lactone "Exaltolide") have been placed on the market as substitutes for the natural musks.


I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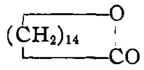
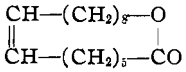
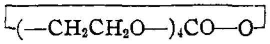

III

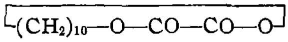

IV

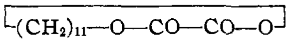
The observations on the anhydrides and carbonates are assembled in Table I, together with Ruzicka's data on the ketones and lactones. It will be noted that in each of the four series, with the possible exception of the ketones, odors are rather vague and indefinite until the number of atoms in the ring reaches 9. A camphoraceous or minty note then appears, and at about 13 atoms a woody or cedar-like quality. Beyond this point there is a nuance of musk which however in the anhydride series does not become definite and pronounced until the 15-atom compound is reached. At 15 or 16 atoms the musk quality approaches a maximum of fullness and homogeneity. Tetradecamethylene carbonate (17 atoms) shows a remarkable resemblance to "Exaltolide" (16-atom lactone). Beyond 18 or 19 atoms the odors in each series practically disappear.

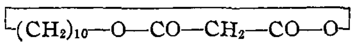
The structural feature common to the four series is the presence of one or more C═O groups as a member of a ring. It is rather extraordinary that the manner in which the C═O group is linked in the ring should make so little difference in the quality of the odor. On the other hand it appears that any modification of the C═O group itself completely changes the odor. Ruzicka, Schinz and Seidel report[3] that the alcohol corresponding to civetone has a faint and only slightly characteristic odor.

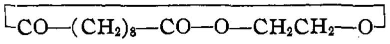
The fact that the only requirement (there are no doubt other limits not yet known) for musk-like odor is the presence of a C═O group in a ring of approximately 15 atoms is further illustrated by the following compounds not included in Table I (other physical properties of these compounds are listed in Table I of Paper XX)

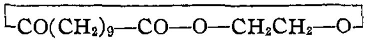

$(-CH_2CH_2O-)_4CO-O$ tetraethylene carbonate, 14 atoms, fresh, faint, musk-like


$(CH_2)_{10}-O-CO-CO-O$ decamethylene oxalate, 14 atoms, fresh, musk-like


$(CH_2)_{11}-O-CO-CO-O$ undecamethylene oxalate, 15 atoms, musk-like


$(CH_2)_{10}-O-CO-CH_2-CO-O$ decamethylene malonate, 15 atoms, faint, musk-like


$CO-(CH_2)_8-CO-O-CH_2CH_2-O$ ethylene sebacate, 14 atoms, musk-like

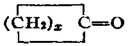
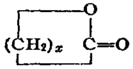
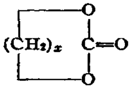
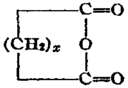

$CO(CH_2)_9-CO-O-CH_2CH_2-O$ ethylene undecanedioate, 15 atoms, musk-like

The first of these contains six oxygen atoms in the ring of which two are directly connected to the carbonyl group; the second and third have two

[3] Ruzicka, Schinz and Seidel, *Helv. Chim. Acta*, **10**, 695 (1927).

TABLE I

ODORS OF CYCLIC COMPOUNDS

| Atoms in ring | Ketones  | Lactones  | Carbonates  | Anhydrides  |
|---|---|---|---|---|
| 5 | Bitter almond and menthol | Fruity | Faint | Odorless |
| 6 | Bitter almond and menthol | Faint[a] | Faint | Odorless |
| 7 | Transition | Faint, spicy and floral[b] | | Faint, pungent |
| 8 | Transition | | | |
| 9 | Camphoraceous | | Minty, empyreumatic | |
| 10 | Camphoraceous | | Minty, less empyreumatic | Spicy |
| 11 | Camphoraceous | | Earthy, camphoraceous | Spicy |
| 12 | Camphoraceous | | Earthy, camphoraceous | Spicy |
| 13 | Cedarwood, then musk | | Cedar, faint rose and camphor | |
| 14 | Musk | Musk | Musk, camphoraceous | Aromatic |
| 15 | Pure musk | Musk and ambergris | Musk | Musk |
| 16 | Transition | Musk | Musk | |
| 17 | Civet | Civet | Musk | |
| 18 | Faint civet | Faint | | |
| 19 | Faint | | | Musk |
| 21 | | | Faint | |

[a] Observation on a specimen very carefully purified by F. J. Van Natta. [b] From unpublished work of F. J. Van Natta. This compound has not yet been described.

adjacent carbonyls to which annular oxygens are attached, in the fourth a methylene has been interposed between the two carbonyls, and in the fifth and sixth eight and nine methylenes are inserted between the carbonyls. It would be of great interest to have information on similar compounds in which the carbonyls are replaced by methylenes; unfortunately macrocyclic ethers are as yet entirely unknown.

From the practical standpoint the cyclic anhydrides are of no interest as odorous materials since they polymerize spontaneously on standing and the odors then disappear. (This fact incidentally demonstrates that the odors of the cyclic anhydrides are not due to any traces of the corresponding cyclic ketones which might conceivably be present as impurities.) On the other hand the cyclic esters, with the exception of the oxalates, are quite resistant to hydrolysis or polymerization and from the practical standpoint they have the advantage over the previously described ketones and lactones that they are formed in relatively high yields.

**Molecular Refractions.**—Ruzicka and Stoll have shown that the molecular refractions of macrocyclic lactones[4] and hydrocarbons[5] are lower by about 0.6 unit than the calculated values. The macrocyclic carbonates exhibit the same peculiar negative exaltation and to about the same degree. Typical data are assembled in Table II.

TABLE II

MOLECULAR REFRACTIONS OF CYCLIC ESTERS

| Compound | Atoms in ring | $M_D$ calcd. | $M_D$ found | $E\ M_D$ |
|---|---|---|---|---|
| Ethylene carbonate | 5 | 17.15 | 16.87 | −0.28 |
| Trimethylene carbonate | 6 | 21.77 | 21.92 | + .15 |
| Octamethylene carbonate | 11 | 44.86 | 44.45 | − .41 |
| Nonamethylene carbonate | 12 | 49.48 | 49.05 | − .43 |
| Decamethylene carbonate | 13 | 54.20 | 53.49 | − .71 |
| Undecamethylene carbonate | 14 | 58.71 | 58.17 | − .54 |
| Dodecamethylene carbonate | 15 | 63.33 | 62.66 | − .67 |
| Tridecamethylene carbonate | 16 | 67.95 | 67.32 | − .63 |
| Tetradecamethylene carbonate | 17 | 72.57 | 71.74 | − .83 |
| Octadecamethylene carbonate | 21 | 91.04 | 91.05 | + .01 |
| Tetraethylene glycol carbonate | 14 | 49.79 | 50.21 | + .42 |
| Decamethylene oxalate | 14 | 58.72 | 59.12 | + .40 |
| Undecamethylene oxalate | 15 | 63.34 | 63.56 | + .22 |
| Decamethylene malonate | 15 | 63.34 | 63.63 | + .29 |

The last four compounds of the table appear to have a positive exaltation, but the amounts of these materials available were quite small and their purity was somewhat uncertain. The compounds for which negative values are listed were for the most part purified by crystallization. No significance can be attached to the fluctuations in these negative values

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[4] Ruzicka and Stoll, *Helv. Chim. Acta*, **11**, 1159 (1928).

[5] Ruzicka, Stoll, Huyser and Boekenoogen, *ibid.*, **13**, 1152 (1930).

from one member of the series to the next since the molecular refractions were not all taken at the same temperature.

**Melting Points.**—The melting points of the known macrocyclic compounds show little regularity in the nature of the change produced by increasing molecular weight but in the range of 8 to 14 atoms there is generally an oscillation from one member to the next.[5] The cyclic carbonates show a similar oscillation, the melting points and ring size for some of the monomeric polymethylene carbonates being

| | | | | | | |
|---|---|---|---|---|---|---|
| 11 | 12 | 13 | 14 | 15 | 16 | 17 |
| 23° | 35° | 11° | 41° | 12° | 25° | 22° |

## Summary

Macrocyclic esters and anhydrides have odors closely resembling those of the ketones and lactones of the same ring size. The rings in the neighborhood of fifteen atoms have musk-like odors. The molecular refractions show a negative exaltation. Melting points in the carbonate series oscillate from one member to the next.

WILMINGTON, DELAWARE

RECEIVED SEPTEMBER 2, 1933
PUBLISHED DECEMBER 14, 1933

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[CONTRIBUTION NO. 134 FROM THE EXPERIMENTAL STATION OF E. I. DU PONT DE NEMOURS & COMPANY]

# Studies of Polymerization and Ring Formation. XXII. Stereochemistry and Mechanism in the Formation and Stability of Large Rings

BY WALLACE H. CAROTHERS AND JULIAN W. HILL

A great deal of discussion has been devoted to stereochemistry and mechanism in the formation of rings, but on account of the limited range of experimental facts available, fruitful discussion has been largely restricted to rings containing fewer than eight atoms. The only important series exemplifying closure of long chains hitherto has been the macrocyclic ketones which Ruzicka obtained by heating salts of the higher dibasic acids. As a basis for theoretical inferences this general reaction suffers from two disadvantages. The macrocyclic ketones are formed in such small yields (0.1 to 5%) that they can hardly be regarded as major reaction products, and the nature of the reaction (thermal destruction at high temperatures) is such that its mechanism is inherently obscure. Data on the polyesters and anhydrides now provide the possibility for a much clearer insight into the mechanism of the formation of large rings.

Following the demonstration of the stable existence of large carbon rings, Baeyer's theory of negative strain has been generally abandoned and replaced by the idea of Sachse and Mohr[1] that large rings may exist in

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(1) Mohr, *J. prakt. Chem.*, **98**, 348 (1918).